

# Thermodynamic Calculations for Molecules with Asymmetric Internal Rotors. II. Application to the 1,2-Dihaloethanes

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Received 14 February 2007; Revised 4 June 2007; Accepted 21 June 2007

DOI 10.1002/jcc.20807

Published online 30 July 2007 in Wiley InterScience (www.interscience.wiley.com).

**Abstract:** The thermodynamic properties of three halocarbon molecules relevant in atmospheric and public health applications are presented from *ab initio* calculations. Our technique makes use of a reaction path-like Hamiltonian to couple all the vibrational modes to a large-amplitude torsion for 1,2-difluoroethane, 1,2-dichloroethane, and 1,2-dibromoethane, each of which possesses a heavy asymmetric rotor. Optimized *ab initio* energies and Hessians were calculated at the CCSD(T) and MP2 levels of theory, respectively. In addition, to investigate the contribution of electronically excited states to thermodynamic properties, several excited singlet and triplet states for each of the halocarbons were computed at the CASSCF/MRCI level. Using the resulting potentials and projected frequencies, the couplings of all the vibrational modes to the large-amplitude torsion are calculated using the new STAR-P 2.4.0 software platform that automatically parallelizes our codes with distributed memory via a familiar MATLAB interface. Utilizing the efficient parallelization scheme of STAR-P, we obtain thermodynamic properties for each of the halocarbons, with temperatures ranging from 298.15 to 1000 K. We propose that the free energies, entropies, and heat capacities obtained from our methods be used to supplement theoretical and experimental values found in current thermodynamic tables.

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**Key words:** thermodynamic properties; halocarbons; internal rotation; large-amplitude torsion; vibrations

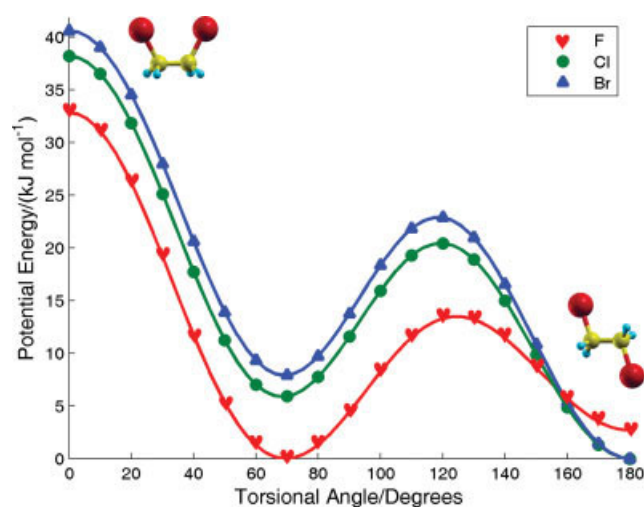
## Introduction

The search for environmentally acceptable alternatives to chlorofluorocarbons (CFCs) has become the focus of much attention since the late 1980s.<sup>1–4</sup> From as early as 1930, CFCs were primarily used as refrigerants and have played an important role in food refrigeration, air conditioning, blowing agents, and solvents.<sup>5</sup> However, it was not until the early 1970s that CFCs were believed to be major contributors to the seasonal ozone depletion over the Antarctic continent.<sup>6–8</sup> In 1987 several governments signed the Montreal Protocol, the first international agreement to protect the global environment, to reduce CFC production significantly by the year 1998. Since then, numerous researchers and industries have set in motion the investigation for new CFC replacements.

Haloethanes, in which one or more halogens have replaced a hydrogen atom, were considered as a potential alternative for CFCs.<sup>9</sup> For example, 1,2-dichloroethane has played a vital role

in industries such as hospitals, steel mills, and air transportation.<sup>10</sup> In 1978, the National Institute for Occupational Safety and Health estimated that over 2 million workers in the United States had been exposed to 1,2-dichloroethane in ~150,000 workplaces.<sup>11,12</sup> The widespread use of these CFC replacements makes it necessary to investigate their reactive properties through kinetic and molecular modeling. Kinetic and molecular models rely on accurate knowledge of thermochemical properties such as entropies, heat capacities, and particularly, free energies. Unfortunately, much of the experimental thermochemical data for the dihaloethanes is unknown, severely limiting the range of compounds whose kinetics and thermochemistry can be accurately predicted. High-resolution spectroscopic investigations are difficult, since the absence of a permanent dipole moment in the most abundant *trans* form in these dihaloethanes prevents measurements

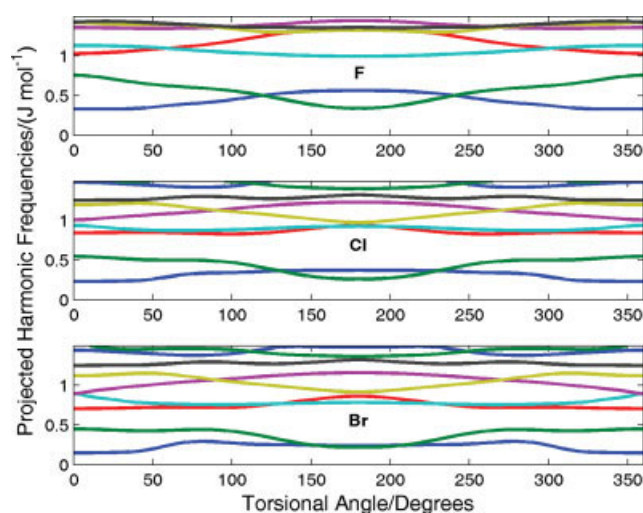
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**Figure 1.** Relaxed *ab initio* torsional potentials of 1,2-difluoroethane, 1,2-dichloroethane, and 1,2-dibromoethane obtained with the cc-pVTZ basis at the CCSD(T)//MP2 level of theory. Both 1,2-dichloroethane and 1,2-dibromoethane have a global energy minimum at the 180° *trans* form, but 1,2-difluoroethane has a *gauche* global energy minimum at 69.7°.

in the microwave region.<sup>13</sup> Complications in infrared spectroscopy are also problematic because of the dense rotational structure from these heavy asymmetric rotors.

For these missing properties, we have chosen a computational quantum chemical approach to study 1,2-difluoroethane, 1,2-dichloroethane, and 1,2-dibromoethane (no thermochemical information exists for 1,2-dibromoethane). The thermochemistries of these dihaloethanes are particularly difficult to estimate, since all of them possess a heavy asymmetric internal rotor. As a result, the geometries and the rotational constants will both be strongly coupled to the internal rotation<sup>14–16</sup> (see, for example, Fig. 3 in this paper). This combination of torsion coupled to overall rotation leads to a break down in conventional thermodynamic formulas. We should also mention a study that is close in spirit to ours is the work by Hnizdo, Darian, and coworkers who



**Figure 2.** Projected harmonic frequencies (up to 1.5 J mol<sup>−1</sup>) for 1,2-difluoroethane, 1,2-dichloroethane, and 1,2-dibromoethane computed as a function of the torsional angle. The lowest frequencies for all cases are significantly coupled to the large-amplitude torsion.

have used Monte Carlo simulations to estimate entropies of internal rotation.<sup>11,17</sup> Their treatment of asymmetric internal rotation utilized a reduced moment of inertia averaged over a thermodynamic ensemble of atomic configurations obtained from stochastic simulations. In this paper, we aim to estimate the missing thermochemical properties from *ab initio* quantum chemical calculations. In a previous publication, we have successfully used a reaction path-like Hamiltonian written in STAR-P parallelized MATLAB<sup>18,19</sup> to obtain free energies, entropies, and heat capacities of butadiene up to 500 K.<sup>20</sup> In this paper, we have modified our computer codes to utilize the new STAR-P 2.4.0 software platform for calculating dihaloethane properties in the 298.15 to 1000 K temperature range. We propose that the thermochemical properties obtained from our methods be used to supplement theoretical and experimental values for the 1,2-dihaloethane molecules.

**Table 1.** Optimized *Ab Initio* Parameters Obtained with the cc-pVTZ Basis at the CCSD(T)//MP2 Level of Theory.

	Global maximum	Global minimum	Local maximum	Local minimum
1,2-Difluoroethane				
Torsional angle (degrees)	0°	69.7°	124.8	180
Potential energy (kJ mol <sup>−1</sup> )	32.86	0	13.49	2.685
1,2-Dichloroethane				
Torsional angle (degrees)	0°	180°	119.4	67.7
Potential energy (kJ mol <sup>−1</sup> )	38.20	0	20.45	5.880
1,2-Dibromoethane				
Torsional angle (degrees)	0°	180°	118.8	68.2
Potential energy (kJ mol <sup>−1</sup> )	40.62	0	22.91	7.915

The potential energy for each molecule is reported relative to its globally lowest minimum.

## Ab Initio Calculations

All ground-state electronic structure calculations for the three halocarbons  $\text{CH}_2\text{X}-\text{CH}_2\text{X}$ , where X stands for F, Cl, and Br, were carried out with the Gaussian 03 package.<sup>21</sup> The relaxed geometry parameters and Hessian matrices were computed using second-order Møller–Plesset perturbation theory (MP2). Coupled cluster with single and double substitutions with perturbative triples (CCSD(T)) single-point energies were subsequently performed at the MP2-optimized geometries. The basis set used for all levels of theory was Dunning's correlation consistent triple-zeta basis, cc-pVTZ.<sup>22</sup> The MP2 geometry optimizations were carried out with extremely tight convergence criteria (root mean square forces = 0.00001 atomic units and root mean square displacements = 0.00004 atomic units) to minimize the low-frequency translational and rotational modes.

The torsional potential at the MP2 level of theory was calculated by constraining the  $\text{X}-\text{C}-\text{C}-\text{X}$  dihedral angle at  $10^\circ$  increments and optimizing all other internal coordinates to minimize the total energy. At all intermediate geometries between the  $\text{C}_{2h}$  *trans* stationary point and the  $\text{C}_{2v}$  *cis* maximum, molecular symmetry was constrained to a  $\text{C}_2$  point group. The CCSD(T)/MP2 torsional potentials relative to the global minimum for each of the three halocarbons are shown in Figure 1, and the parameters characterizing the stationary points are given in Table 1. A complete geometry optimization places the global energy minimum of both 1,2-dichloroethane and 1,2-dibromoethane at a *trans* isomeric form with  $\text{C}_{2h}$  point group symmetry. In striking contrast, the torsional potential of 1,2-difluoroethane exhibits a “*gauche* effect”—the anomalous property of a *gauche* configuration having a lower electronic energy than the *trans* form.<sup>23,24</sup> Using *ab initio* methods, Wiberg previously investigated the *gauche* effect for 1,2-difluoroethane and explained this effect in terms of unfavorable overlap of molecular orbitals in the *trans* configuration.<sup>25,26</sup> According to Wiberg's model, the highly electronegative fluorine atom causes an increased p character in the C–F bond. Consequently, this relatively high p character results in a weaker C–C bond with reduced overlap in the *trans* form as compared to the *gauche* form. Significant changes in electronic structure associated with other types of large-amplitude motion have also been reported in the literature.<sup>27</sup> We should mention that the 6-31G(d) basis set (which was not used for any of the calculations reported here) does not reproduce the 1,2-difluoroethane *gauche* effect and is not even qualitatively correct. This anomalous *gauche* effect, however, is verified with our CCSD(T)/MP2 level of theory, and we recom-

mend using Dunning's correlation consistent basis sets for accurately calculating 1,2-dihaloethane torsional potentials.

It should also be remembered that the ordering of the projected frequencies by diagonalization of the projected force constant matrix is arbitrary for each value of the dihedral angle. Introducing factors of  $-1$  and relabeling eigenvectors to maximize consecutive dot products generates a set of physically meaningful diabatic frequencies and orthogonal vibrational modes.<sup>28</sup> It is essential to obtain the correct ordering of frequencies and eigenvectors, since it provides a correct model for the couplings between the torsional motion and other vibrational modes. Figure 2 shows the variation of the projected harmonic frequencies (up to  $1.5 \text{ J mol}^{-1}$ ) as a function of the internal coordinate path for each of the three halocarbons. In other words, the projected harmonic wave numbers are not constant with respect to  $s$ , indicating a mixing of pure torsion with the other vibrational modes.

In addition to calculations on the ground-state torsional potential, electronically excited singlet and triplet states were computed to determine the major electronic configurations which contribute to thermodynamic properties. All *ab initio* excited state calculations for each of the three halocarbons were carried out with the Molpro 2006.1 package<sup>29</sup> using the complete active space self-consistent field (CASSCF) method<sup>30–32</sup> followed by multireference configuration interaction (MRCI).<sup>33,34</sup> The CASSCF/MRCI method provides an accurate description of excited state energies which cannot be sufficiently described by CCSD(T) single-reference methods. However, the penalty of using the CASSCF/MRCI treatment is an enormous increase in computational time. Therefore, we have computed only the lowest singlet and triplet states in each distinct electronic symmetry for 1,2-difluoroethane, 1,2-dichloroethane, and 1,2-dibromoethane at the *trans* minimum configuration. In the *trans* molecular geometry ( $\text{C}_{2h}$  symmetry), only four electronic states are possible:  $\text{A}_g$ ,  $\text{A}_u$ ,  $\text{B}_u$ , and  $\text{B}_g$ . At the MP2-optimized geometry described previously, CASSCF/MRCI single-point energies were performed on the following singlet and triplet states for each of the halocarbons:  $^1\text{A}_g$ ,  $^1\text{A}_u$ ,  $^1\text{B}_u$ ,  $^1\text{B}_g$ ,  $^3\text{A}_g$ ,  $^3\text{A}_u$ ,  $^3\text{B}_u$ , and  $^3\text{B}_g$ . For all calculations based on the CASSCF method, an active space consisting of 26 electrons in 14 orbitals was used with the cc-pVTZ basis. Finally, MRCI calculations were subsequently performed on the CASSCF wavefunction by including all single and double excitations within the CASSCF active space. The excitation energies (relative to the lowest  $^1\text{A}_g$  electronic state) for all eight singlet and triplet states of 1,2-difluoroethane, 1,2-dichloroethane, and 1,2-dibromoethane are collected in Table 2. A comparison of energies for the three halocarbons indicates

**Table 2.** Energies (Relative to the  $^1\text{A}_g$  Ground State) of the Three 1,2-Dihaloethanes Calculated at the *trans* Molecular Geometry.

	Relative energy ( $\text{kJ mol}^{-1}$ )							
	$^1\text{A}_g$	$^1\text{A}_u$	$^1\text{B}_u$	$^1\text{B}_g$	$^3\text{A}_g$	$^3\text{A}_u$	$^3\text{B}_u$	$^3\text{B}_g$
1,2-difluoroethane	0	1070	1023	1151	1230	1035	965.4	1116
1,2-dichloroethane	0	876.5	852.4	861.0	850.7	834.5	786.1	815.1
1,2-dibromoethane	0	744.0	730.1	724.3	707.8	705.9	667.0	683.3

All energies were computed at the CASSCF/MRCI level of theory with the cc-pVTZ basis.

that a triplet state ( $^3B_u$ ) is the second lowest electronic state for all cases. However, even for 1,2-dibromoethane, where this excitation energy is the smallest of all the halocarbons ( $667.0 \text{ kJ mol}^{-1}$ ), this excited state will only be appreciably populated at a temperature of  $T = (667.0 \text{ kJ mol}^{-1})/R = 80,222 \text{ K}$ . Therefore, the thermodynamic properties derived in this work are accurately described by a single-reference CCSD(T) configuration, and the inclusion of electronically excited states is unnecessary. Consequently, the following section only utilizes the CCSD(T)/MP2 torsional potentials to obtain thermodynamic properties for the three halocarbons within the 298.15 to 1000 K temperature range.

### Quantum Mechanical Partition Function

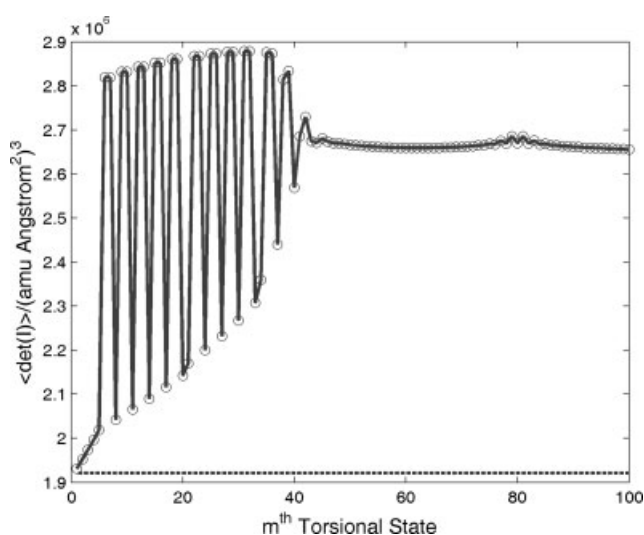
The canonical partition function  $Q(T)$  is the principal quantity used to connect quantum chemical calculations with crucial technological parameters (free energies, entropies, and heat capacities) via statistical thermodynamics. A partition function derived from incorporating the couplings of all the vibrational modes to a large-amplitude torsion has already been reported.<sup>20,35</sup> This modified partition function was based on the reaction path Hamiltonian by Miller et al.,<sup>36</sup> and the thermodynamic properties obtained from this approach were shown to be significantly more accurate compared to other conventional methods. The resulting expressions are briefly reviewed here, and only the slight modifications used in the present work will be described in detail.

The canonical partition function for a large-amplitude torsion coupled to  $3N - 7$  vibrational modes is given by

$$Q(T) = \sum_m \left[ \exp(-E_m/k_B T) q_{\text{rot},m}(T) \prod_{k=1}^{3N-7} q_{\text{vib},m,k}(T) \right], \quad (1)$$

where  $E_m$  is an eigenvalue corresponding to the large-amplitude torsion eigenfunction  $\psi_m(s)$  determined by solving the following matrix equation:

$$\langle \psi_l(s) | \frac{1}{2} \hat{p}_s I_{0ss}^{-1} \hat{p}_s + \frac{1}{2} \mu^{1/4} \left( \hat{p}_s I_{0ss}^{-1} \mu^{-1/2} \left( \hat{p}_s \mu^{1/4} \right) \right) + V_0(s) + \frac{\hbar}{2} \sum_{k=1}^{3N-7} [\omega_k(s) - \omega_k(s_0)] | \psi_m(s) \rangle - \delta_{lm} E_m = 0. \quad (2)$$



**Figure 3.** The lowest 100 effective products of inertia for 1,2-dichloroethane obtained by averaging  $\det[\mathbf{I}_0(s)]$  across the torsional wavefunctions [cf. eq. (7)]. The broken line indicates the numerical value of the equilibrium products of inertia  $I_{0a}I_{0b}I_{0c}$  calculated at the *trans* global minimum. For  $m > 43$ ,  $\det[\mathbf{I}_0(s)]$  is 38% larger than the equilibrium products of inertia.

The operators in eq. (2) are expressed in terms of the large-amplitude torsional coordinate  $s$ , its conjugate momentum  $\hat{p}_s (= -i\hbar\partial/\partial s)$ , the energy along the internal coordinate path  $V_0(s)$ , and the frequencies  $\omega_k(s)$  obtained by diagonalization of a projected Hessian matrix in the  $3N - 7$  small-amplitude degrees of freedom. The variable  $s_0$  is the value of the internal coordinate corresponding to the most stable conformer of the molecule; i.e.  $V_0$  has a global minimum at  $s = s_0$ . The other scalar terms  $I_{0ss}^{-1}$  and  $\mu$  are given by

$$I_{0ss}^{-1}(s) = \left( \sum_{i=1}^N \mathbf{a}'_i(s) \cdot \mathbf{a}'_i(s) \right)^{-1}, \quad (3)$$

$$\mu(s) = I_{0ss}^{-1} \cdot \det(\mathbf{I}_0^{-1}), \quad (4)$$

**Table 3.** Comparison of Free Energy Values for the Three 1,2-Dihaloethanes at Various Temperatures.

	298.15 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
1,2-Difluoroethane									
$G^{\text{Calc}}$ (kJ mol $^{-1}$ )	-71.2	-71.7	-101.5	-133.2	-166.8	-202.2	-239.1	-277.5	-317.4
$G^{\text{Exp}}$ (kJ mol $^{-1}$ )	-71.5	-72.0	-102.0	-134.1	-168.1	-203.8	-241.2	-280.2	-320.6
1,2-Dichloroethane									
$G^{\text{Calc}}$ (kJ mol $^{-1}$ )	-74.7	-75.2	-106.9	-140.9	-176.9	-214.7	-254.3	-295.5	-338.2
$G^{\text{Exp}}$ (kJ mol $^{-1}$ )	-74.9	-75.4	-107.3	-141.5	-177.7	-215.9	-255.9	-297.4	-340.5
1,2-Dibromoethane									
$G^{\text{Calc}}$ (kJ mol $^{-1}$ )	-80.2	-80.8	-114.6	-150.8	-189.1	-229.3	-271.3	-315.0	-360.1

<sup>Calc</sup> Computed values derived from eqs. (1–6) and (8).

<sup>Exp</sup> Literature values obtained from ref. 34.

**Table 4.** Comparison of Entropy Values for the Three 1,2-Dihaloethanes at Various Temperatures.

	298.15 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
1,2-Difluoroethane									
$S^{\text{Calc}}$ (J K <sup>-1</sup> mol <sup>-1</sup> )	286.7	287.1	307.9	327.0	344.8	361.5	377.1	391.7	405.4
$S^{\text{Exp}}$ (J K <sup>-1</sup> mol <sup>-1</sup> )	288.8	289.2	310.7	330.4	348.8	366.0	382.0	397.1	411.2
1,2-dichloroethane									
$S^{\text{Calc}}$ (J K <sup>-1</sup> mol <sup>-1</sup> )	304.3	304.8	328.6	350.0	369.6	387.5	404.1	419.4	433.7
$S^{\text{Exp}}$ (J K <sup>-1</sup> mol <sup>-1</sup> )	305.9	306.3	330.6	352.5	372.5	390.9	407.8	423.5	438.2
1,2-Dibromoethane									
$S^{\text{Calc}}$ (J K <sup>-1</sup> mol <sup>-1</sup> )	324.8	325.3	350.2	372.6	392.9	411.4	428.4	444.0	458.6

<sup>Calc</sup>Computed values derived from eqs. (1–6) and (9).<sup>Exp</sup>Literature values obtained from ref. 34.

and  $\mathbf{I}_0$  is the normal  $3 \times 3$  Cartesian inertia tensor along the path. The vectors  $\mathbf{a}_i (= m_i^{1/2} \mathbf{r}_i)$  are the mass-weighted Cartesian coordinates of the  $i$ th atom at a point on the path  $s$  with respect to the Eckart axis system, and  $\mathbf{a}'_i = d\mathbf{a}_i/ds$ . One also requires the following definitions to completely define eq. (1):

$$q_{\text{vib},m,k}(T) = \frac{1}{1 - \exp\{-\hbar[\omega_k(s_0) + \langle \psi_m(s) | \omega_k(s) - \omega_k(s_0) | \psi_m(s) \rangle] / k_B T\}} \quad (5)$$

$$q_{\text{rot},m}(T) = \frac{1}{\sigma} \left( \frac{2k_B T}{h^2} \right)^{3/2} \{ \pi \langle \psi_m(s) | \det[\mathbf{I}_0(s)] | \psi_m(s) \rangle \}^{1/2}, \quad (6)$$

where the variable  $\sigma$  ( $= 2$  for all three cases) is the rotational symmetry number which prevents overcounting of indistinguishable configurations in classical phase space. The partition function in eq. (6) approximately takes into account the coupling between internal and external rotation by replacing the equilibrium products of inertia  $I_{0a}I_{0b}I_{0c}$  by the torsional-averaged quantity

$$I_{\text{eff},m} = \langle \psi_m(s) | \det[\mathbf{I}_0(s)] | \psi_m(s) \rangle. \quad (7)$$

Since the rotational constants depend strongly on the internal rotation coordinate for asymmetric rotors, this effect can be incorporated by evaluating the determinant of the inertia tensor averaged over the large-amplitude wavefunctions.<sup>37</sup>

Figure 3 shows the variation of  $I_{\text{eff},m}$  in eq. (7) for the lowest 100 torsional states of 1,2-dichloroethane. The dotted horizontal line is the numerical value for the rigid rotor products of inertia  $I_{0a}I_{0b}I_{0c}$  evaluated at the *trans* conformation. For  $5 < m < 43$ ,  $I_{\text{eff},m}$  varies rapidly between two limits, since the torsional wavefunction alternates between the two *gauche* local minima and the single *trans* minimum. For  $m > 43$ , the torsion is nearly a free rotation, and  $I_{\text{eff},m}$  is approximately constant with a limiting value of  $2.66 \times 10^6$  (amu  $\text{\AA}^2$ )<sup>3</sup>. Figure 3 indicates the value of  $I_{\text{eff},m}$  is 38% larger than the equilibrium products of inertia  $I_{0a}I_{0b}I_{0c}$  when  $m > 43$ ; therefore, using the conventional rigid rotor inertias may incur significant errors in the external rotational partition function alone. In the following section, we utilize eqs. (1–6) to obtain thermochemical properties for each of the three halocarbons.

## Thermodynamic Calculations and Results

The partition functions for 1,2-difluoroethane, 1,2-dichloroethane, and 1,2-dibromoethane were obtained by numerical summation over the lowest 20,001 large-amplitude torsion eigenvalues defined in eq. (1). A large set of energy eigenvalues is

**Table 5.** Comparison of Heat Capacity Values for the Three 1,2-Dihaloethanes at Various Temperatures.

	298.15 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
1,2-Difluoroethane									
$C_P^{\text{Calc}}$ (J K <sup>-1</sup> mol <sup>-1</sup> )	65.5	65.8	79.3	92.2	103.3	112.7	120.7	127.5	133.3
$C_P^{\text{Exp}}$ (J K <sup>-1</sup> mol <sup>-1</sup> )	67.7	67.9	82.0	95.2	106.6	116.1	124.1	131.0	136.8
1,2-Dichloroethane									
$C_P^{\text{Calc}}$ (J K <sup>-1</sup> mol <sup>-1</sup> )	75.9	76.2	90.0	102.2	112.2	120.5	127.3	133.2	138.2
$C_P^{\text{Exp}}$ (J K <sup>-1</sup> mol <sup>-1</sup> )	77.3	77.6	91.8	104.4	114.9	123.3	130.4	136.3	141.3
1,2-Dibromoethane									
$C_P^{\text{Calc}}$ (J K <sup>-1</sup> mol <sup>-1</sup> )	79.0	79.3	94.1	106.4	116.1	123.9	130.3	135.7	140.4

<sup>Calc</sup>Computed values derived from eqs. (1–6) and (10).<sup>Exp</sup>Literature values obtained from ref. 34.

required so that the error due to the limited number of states included in the partition function is negligible for the higher temperatures of interest. The corresponding set of eigenvectors is also necessary in this computation in order to calculate the modified vibrational and rotational partition functions defined in eqs. (5) and (6), respectively. As a result, these massive computations were performed in a highly parallelized manner with MATLAB software enabled by the STAR-P 2.4.0 interactive parallel computing platform provided by Interactive Supercomputing. Detailed descriptions of STAR-P and its software architecture have been given by Choy and Edelman.<sup>18,19</sup> For the present work on the halocarbons, a large set of eigenvalues and eigenvectors defined in eq. (2) were computed by diagonalizing a double-precision, non-sparse  $20,001 \times 20,001$  matrix.

Once the eigenvalues and eigenvectors have been computed, the thermodynamic functions for the Gibbs free energy, entropy, and heat capacity can be directly calculated from the canonical partition function:

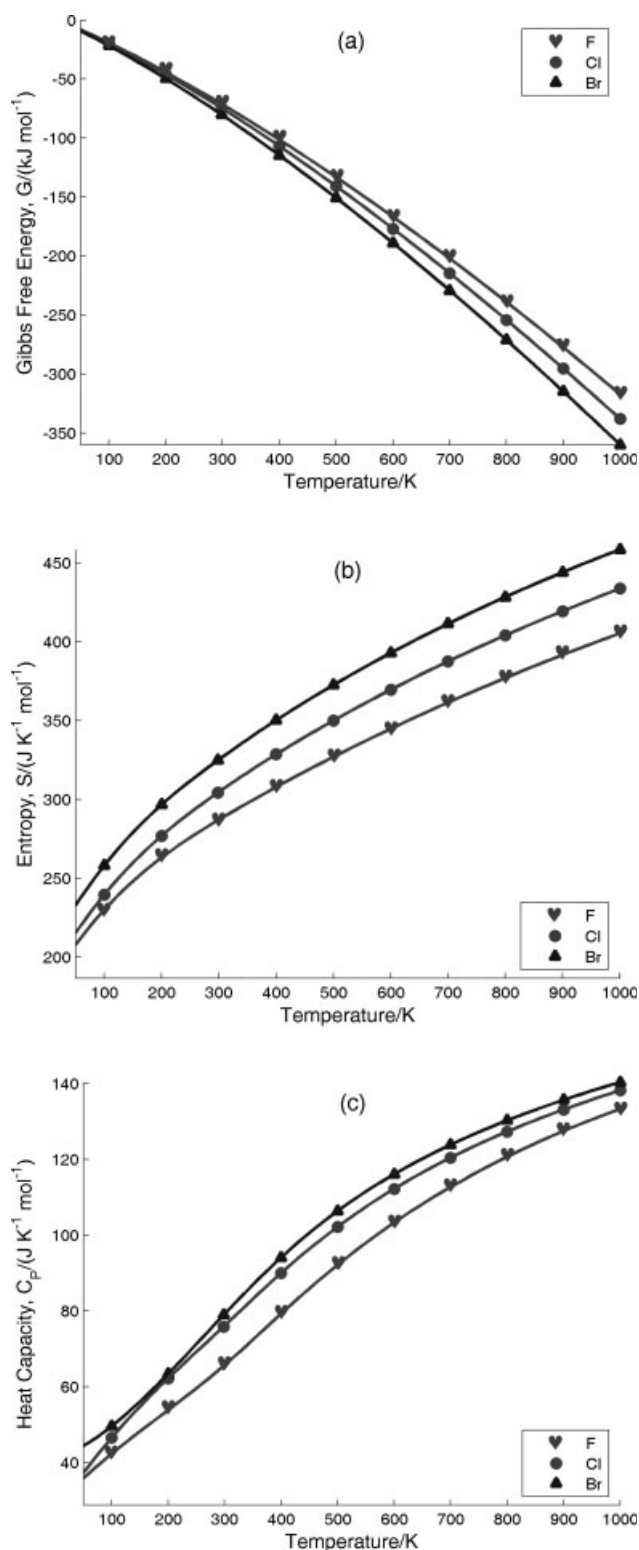
$$G(T) = -RT \ln[Q(T)], \quad (8)$$

$$S(T) = R \ln[Q(T)] + RT \frac{\partial \ln[Q(T)]}{\partial T}, \quad (9)$$

$$C_p(T) = 2RT \frac{\partial \ln[Q(T)]}{\partial T} + RT^2 \frac{\partial^2 \ln[Q(T)]}{\partial T^2} + R, \quad (10)$$

where  $R$  is the ideal gas constant and  $Q(T)$  implicitly includes a contribution due to translation which is always separable from vibration and rotation. The numerical values of  $G(T)$ ,  $S(T)$ , and  $C_p(T)$ , each computed for 1,2-difluoroethane, 1,2-dichloroethane, and 1,2-dibromoethane, are given in Tables 3–5 and also shown in Figures 4 (a–c). The experimental values recommended by the Thermodynamics Research Center<sup>38</sup> found in standard thermodynamic reference data are also given for 1,2-difluoroethane and 1,2-dichloroethane. The data compiled in the standard thermodynamic references are sometimes obtained by averaging several experimentally calculated values; as a result, the error for each data set is difficult to quantify, and the reference data should not be expected to be better than 1% from the best experimental results.

Based on our values, the calculated entropies and heat capacities are quite reliable and usually good to within  $1 \text{ cal K}^{-1} \text{ mol}^{-1}$ . The derived thermodynamic properties generally underestimate the values available from experiment, but the agreement between the calculated and experimental data is generally good. This small discrepancy can be associated with the anharmonic couplings of the other  $3N - 7$  modes to the torsion which have only been treated perturbatively in this work. It is clear that it may be necessary to consider the low-frequency CCX bending motions (where X stands for F, Cl, and Br) to obtain better estimates of thermodynamic properties. To our knowledge, the experimental thermochemical properties of 1,2-



**Figure 4.** (a–c). Free energies, entropies, and heat capacities for 1,2-difluoroethane, 1,2-dichloroethane, and 1,2-dibromoethane computed as a function of temperature.

dibromoethane have not been studied and remain unknown. Experimental measurements on the heat of formation for 1,2-dibromoethane would be extremely valuable as a check on the accuracy of the theoretical calculations.

## Conclusions

A computational method based on the internal coordinate path kinetic energy operator with an *ab initio* potential energy surface was employed to determine the thermochemical properties of 1,2-difluoroethane, 1,2-dichloroethane, and 1,2-dibromoethane. Our treatment, which uses the new STAR-P 2.4.0 interactive parallel computing platform, is practical and accurate for routine thermochemical calculations on large polyatomic systems. Having these programs written in a familiar high-level language permits easy modification of existing codes for applications with even larger systems. To our knowledge, this is the first computational study in the literature on the thermochemical properties of 1,2-dibromoethane. These new values for free energies, entropies, and heat capacities help extend the range of dihaloethanes that can be included in kinetic models of atmospheric degradation and combustion.

The MATLAB scripts used to run the STAR-P 2.4.0 interactive parallel computing platform can be obtained upon request from the corresponding author.

## Acknowledgments

All *ab initio* calculations were performed on a custom-built server at the Sidney-Pacific Residence at the Massachusetts Institute of Technology, which comprises two processors ( $2 \times 2.8$  GHz Intel Xeon), with a total of 4 Gb of RAM. All other calculations and algorithm developments were performed on a parallelized version of MATLAB using STAR-P 2.4.0 from Interactive Supercomputing. The authors are grateful to Prof. Alan Edelman and Dr. Christopher Hill for generous use of their computational facilities at M.I.T.

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